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Monte Carlo simulations of confined hard sphere fluids*

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We describe a grand-canonical Monte Carlo simulation of a hard sphere fluid confined to porous media with arbitrary pore shape. The pore geometry is given by a triangulated surface representation of the solid-void interface. This algorithm is developed to study the dependence of thermodynamic quantities, such as the average density and adsorption, on the shape of the pore. Particular pore shape geometries that are analysed are the labyrinthine domains bounded by so-called triply-periodic minimal surfaces.

1. Introduction

The statistical physics of bulk properties of simple fluids, that is fluids in containers of infinite size, are well understood [5,7]. In contrast, the properties of spatially confined fluids, for example in porous media or in biological cells or networks, are subject of current research. Several critical phenomena, such as capillary condensation, are the consequence of confinement of a fluid in containers of nano- or micrometer scale where the fluid senses the influence of the substrate [2,3]. However confinement also affects non-critical properties of the fluids. Rather the thermodynamic potentials (that determine the equilibrium properties of the fluid) are dependent on the shape or morphology of the confining domain. For example, the grand-canonical partition function Ω, that for bulk fluids is a function of the container size V available to the particles, of the chemical potential μ and of the temperature T, becomes a function of the shape of the confining domain S. For the situation where the fluid correlation length ξ is substantially smaller than the domain sizes and for confining domains that are represented by the complement of convex bodies, it has recently been argued (and evidence given by density functional theory [9,8]) that

$$\Omega[S,\mu,T] = -p\,V[S] + \sigma\,A[S] + \kappa\,\mathcal{H}[S] + \overline{\kappa}\,\chi[S]. \tag{1}$$

Here $V[S]$ is the volume of S, $A[S]$ the surface area of its bounding surface ∂S, $\mathcal{H}[S]$ the integrated mean curvature of ∂S and $\chi[\partial S]$ the integrated Gaussian curvature of ∂S, i.e. the topological Euler index. The coefficients p, σ, κ and $\overline{\kappa}$ are independent of S but depend on T and μ. The four morphological measures V, A, $\mathcal{H}$ and χ are known as Minkowski functionals and are known to provide a complete morphological characterisation of the shape of a body S with respect to additive, continuous and motion-invariant

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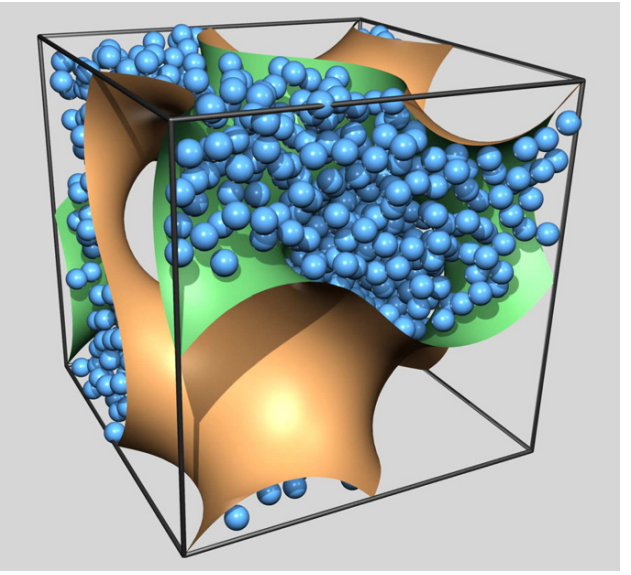

Figure 1. Snapshot of a hard sphere liquid confined to one of the domains given by the Gyroid minimal surface of cubic symmetry $I4_132$ with lattice size $L = 17$. The cubic frame is the simulation box $\mathbb{P} = [0, L]^3$ that corresponds to the cubic translational unitcell of the surface.

functionals $f(S)$ [4,10,11]. This implies that $\Omega[S, \mu, T]$ is an additive functional of S. These studies considered only domains S that were the complement of a convex body, implying that the effect of the substrate-fluid interaction can decay to the bulk density at large distances from the substrate. Here we describe the implementation of a Monte Carlo approach that will allow to verify the validity of morphological relationships such as Eq. (1) for porous geometries of arbitrary shape.

The system studied here is an ensemble of three-dimensional hard spheres of constant diameter $\sigma := 2R = 1$ whose centers are restricted to the interior of a pore. In particular, the pore may one of the two domains bounded by a triply-periodic minimal surface, e.g. the Gyroid [12], in which case the pore is periodic with three perpendicular lattice vectors of length a. The complement of the pore is solid, and not accessible to the spheres (The spheres centers are constraint to the pore S and must have a distance of at least one sphere radius R to the solid-pore interfacial surface). In the case of the Gyroid the pore and the complement are mirror images of one another, both with volume fraction of exactly 50%. See Fig. 3. The challenge is to ensure that each sphere-sphere or sphere-solid overlap test only take $\mathcal{O}(1)$ time.

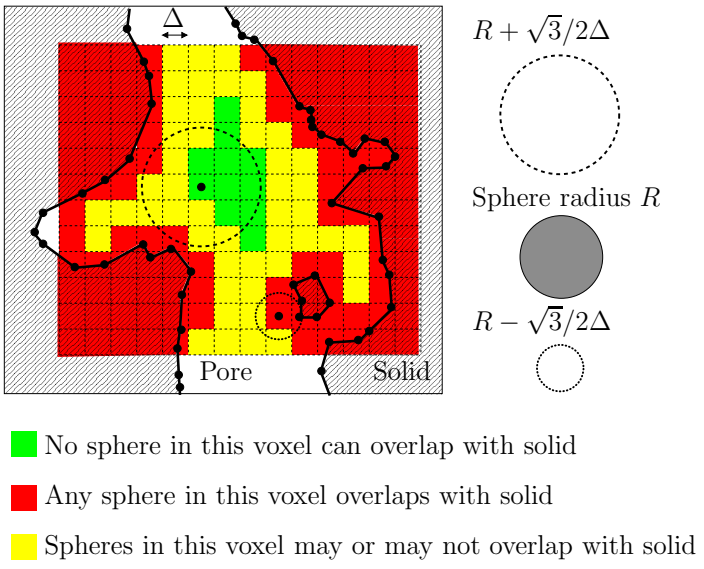

Figure 2. Look-up table for fast but exact test whether a hard sphere of radius R overlaps with the solid phase or not. See text for details.

2. Simulation of confined fluids

We perform standard Metropolis Grand Canonical Monte Carlo simulation of hard spheres as described by [5], and based on original work by Adams [1]. The confinement by the pore is modelled by a sphere-solid potential that is 0 for a sphere center position without overlap with the solid and infinity otherwise. Results are presented as function of the excess chemical potential μ_{ex} (instead of the chemical potential μ as μ_{ex} conceals the dependence on particle mass). The temperature is constant $k_B T = 1$.

The solid phase is represented by a triangulated representation of the solid-pore interface, consisting in vertices connected by triangles (The triangles are oriented such that the triangle normal vectors point into the pore space). For both insertion and translation Monte Carlo moves the test if a sphere overlaps with the solid is time-consuming. A basic implementation of the test whether a sphere of radius R at a given position $\vec{r}$ overlaps with the solid phase identifies the nearest triangle to $\vec{r}$, and analyses the signed distance from $\vec{r}$ to the triangle. If its negative (meaning inside the solid phase) or smaller than R (meaning in the pore phase but too close to the pore/solid interface) a sphere at $\vec{r}$ is not fully contained in the pore domain, otherwise it is. The search for the nearest triangle is a slow operation, and our implementation improves on this scheme by introducing a precomputed cubic grid lookup table, see Fig. 2, where each voxel has either of the following status: (a) voxel in solid phase or so close to the interface that any sphere of radius R positioned anywhere in the voxel overlaps with solid, (b) voxel so deep in pore phase that

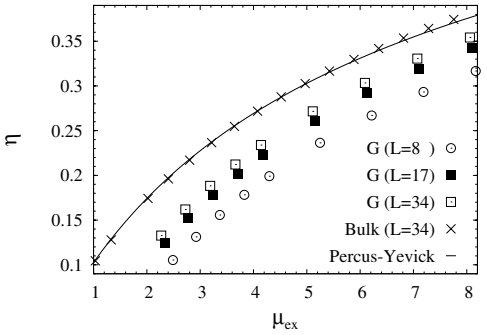

Figure 3. Average fluid density η as function of the excess chemical potential μ_{ex} for hard spheres confined to one of the two labyrinthine domains of the triply-periodic Gyroid surface with lattice length L (the sphere diameter is 1). Also shown are Monte Carlo results for the bulk hard sphere fluid without confining geometry and the functional form for $\eta(\mu_{ex})$ in the Percus-Yevick approximation.

all spheres positioned anywhere in the voxel are fully contained in pore, and (c) spheres in this voxel may or may not overlap with solid depending on their exact position. For case (c), the voxel also specifies a list of those triangles that may overlap with spheres in this voxel; the basic test described above needs to be applied only to these spheres.

3. Hard spheres confined by the Gyroid triply-periodic minimal surface

To illustrate this method we extract the average density $\eta = \langle N \rangle \frac{4\pi R^3}{3}/(\phi V)$ for spheres confined in one of the labyrinthine domains bounded by the Gyroid triply-periodic minimal surface with lattice length L from a simulation [12]. For a given μ_{ex}, $\langle N \rangle$ is the thermodynamically averaged number of spheres in the system and $\phi = 50\%$ the fraction of the volume V of the simulation box $[0, L]^3$ inside the pore space (hence, ϕV is the pore volume), see Fig. 3.

Simulations of spheres confined by the Gyroid were carried out for translational vector length $L = 8, 17, 34$ with approximately 20 independent runs, each of approximately 10000 Monte Carlo updates per sphere. Furthermore a bulk system, i.e. without confining surface, was simulated and yields values of η very close to the Percus-Yevick approximation for the function $\eta(\mu_{ex})$ [7]. As expected, the packing fraction η in the Gyroid domains deviates more from the bulk behaviour for small translational vector L than for larger L. This can be understood, as L only changes the length scale of the system. For large L the pore is larger relative to the sphere radius than for smaller L and the influence of the confining substrate is smaller. Additionally, we have asserted that finite size effects are small by simulating in $2 \times 2 \times 2$ translational units of the Gyroid surface but with

the same translational lattice vector, i.e. in systems with the same domain size or length scale but 2^3 times the volume.

4. Conclusion

We have described an implementation of grand-canonical Metropolis Monte Carlo simulations for hard sphere fluids confined in pores of arbitrary geometry given by triangulations of the solid void interface. For fast simulation times (only approximately a factor 10 slower than for an unconfined fluid) we have implemented a look-up table. The results obtained with this method for the fluid density η of a fluid confined in the Gyroid structure at different length scales L appear physically reasonable.

Using this numerical approach we intend to analyse the range of validity of morphometric formulae, such as in Eq. (1), by systematically analysing large classes of triply-periodic minimal surface geometries [13] and other pore geometries. Triply-periodic minimal surfaces are generic models for pore geometries with negatively curved pore geometries, and are also motivated by their realisations as nanoscopic spatial structures in self-assembled structures, for example in some butterfly wings [6].

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